A METHOD FOR PREPARING A CHLORINE DIOXIDE BLOCK-REMOVING AGENT IN OIL WELLS

FIELD OF THE INVENTION

The present invention relates to a method for preparing a chlorine dioxide block-removing agent in oil wells.

BACKGROUND OF THE INVENTION

Petroleum production is a complex systems engineering relating to various knowledge. The key point of the petroleum production engineering is to keep the water well and the oil well unblocked, so as to keep oil continuously extracted out with water continuously injected in. Unfortunately, the oil well and the water well are blocked very often. There are four kinds of blocking substances: the first one is inorganic salts (such as carbonates, silicates, etc.); the second one is biological coenobiums; the third one is the ferrous sulfide blocker in oil layers produced by steel corrosion induced by the biological coenobiums; the fourth one is the high molecular polymers used in well drilling, well pressing, well repairing, press-fraction and water packing-off in the tertiary oil extraction procedures, those high molecular polymers will damage the permeability of the subterranean in different degree and form blocking.

At present, the acidic solution used in acidification block-removing technology is corrosive to minerals in subterranean and to inorganic blocks in different degree; this corrosion can release mostly permeability damage included by inorganic substances, but it is less effective, even though no effective to blockings induced by polymers and microorganisms.

According to the disclosures of some literatures, the chlorine dioxide was already

used to remove blockings in oil fields in the end of 1980's in the USA and other countries. It has obtained outstanding effects on oil output increase and blocking-removing. In China, lots of fields and research institutes also did lots of work on block-removing by way of chlorine dioxide in oil fields in 1990's. However, due to the danger of explosion induced by the leak of chlorine dioxide, the damage for the human body, and the corrosion to the equipments and pipes in oil fields induced by the strong oxidization of chlorine dioxide, it has not been applied in real oil fields yet.

OBJECT OF THE INVENTION

The object of the present invention is to overcome the shortcomings in the prior art to provide a method for preparing a chlorine dioxide block-removing agent in the oil wells. By way of the strong oxidizability of chlorine dioxide produced in the oil, it can degrade the polymers, such as polyacrylamide, sesbania and guanidine etc., to lower the viscosity thereof and to improve their flowability to make them flow out easily, and also can quickly kill various microorganisms. Therefore, the blockings in oil wells and water wells can be removed.

SUMMARY OF THE INVENTION

The present invention relates to a method for preparing chlorine dioxide block-removing agent in oil wells, which comprises:

a. providing a tank 1, adding chlorates or stable chlorine dioxide and water into the tank 1 to make them dissolved in the tank 1 thoroughly;
b. providing a tank 2, adding acidic substances, which can be dissolved in water and produce hydrogen ion in an aqueous solution, and water into the tank 2 to make them dissolved in the tank 2 thoroughly;
c. providing a high pressure injection pump 3. which is provided with a water-feeding pipe 4 and a water-outgoing pipe 5; the said water-feeding water

pipe 4 being directly connected with the tank 1, and connected with the tank 2 through a pressure pump 7 provided on the tank 2;

d. initiating the high pressure injection pump 3 and the pressure pump 7, making the solution in the tank 1 and the solution in the tank 2 entered into the high pressure injection pump 3 via the water-feeding pipe 4 and being pressured in the pump 3, then the mixed solution being entered into the oil (water) well 6 via the water-outgoing pipe 5 of high pressure injection pump 3, thereby the chlorine dioxide block-removing agent being synthesized in the well by the reaction between the chlorates and the acidic substances which can be dissolved in water and produce hydrogen ion in the aqueous solution.

According to the method of the present invention, wherein, the concentration of the aqueous solution of said chlorine dioxide block-removing agent synthesized in the well is controlled in the range of about 200mg/L to 5000mg/L.

According to the method of the present invention, wherein, the mix of the chlorate aqueous solution and acidic substances aqueous solution can be carried out at any position of the water-feeding pipe 4 of the high pressure injection pump 3.

According to the method of the present invention, wherein, the said chlorate is selected from the group consisting of the chlorates of mono-valence and bi-valence metal cations and the chlorites of mono-valence and bi-valence metal cations.

According to the method of the present invention, wherein, the chlorates include sodium chlorate and potassium chlorate; the chlorites include sodium chlorite and potassium chlorite.

According to the method of the present invention, wherein, the said acidic substances are selected from the group consisting of the monoacids, biatomic acids and ternary acids which can be dissolved in water and can produce hydrogen ion, and the acid

inorganic and organic salts which can be dissolved in water and can produce hydrogen ion.

According to the method of the present invention, wherein, the said monoacids include chloric acid, hydrofluoric acid, sulfamic acid, formic acid, lactic acid and acetic acid; the said biatomic acids include oxalic acid and tartaric acid; the said ternary acids include phosphoric acid and citric acid; the said acid salts include acid sulfate, acid phosphorate, acid carbonate and acid tartarate.

According to the method of the present invention,wherein, the acid is phosphoric acid and the acid salts are bi-sodium phosphorate, sodium phosphorate or sodium tartarate.

BRIEF DESCRIPTION OF THE DRAWING

Figure 1 shows the arrangement of the apparatus used in the method of the present invention, wherein, number 1 represents the tank for main materials; number 2 represents the tank for adjuvant materials; number 3 represents the high pressure injection pump; number 4 represents the water-feeding pipe of the high pressure injection pump; number 5 represents the water-outgoing pipe of the high pressure injection pump; number 6 represents an oil (water) well; number 7 represents a pressure pump; and number 8 represents an adjuvant flow meter.

DETAILED DESCRIPTION OF THE INVENTOIN

The present invention provides a method for preparing chlorine dioxide block-removing agent in oil wells, which comprises:

a. providing a tank 1, adding chlorates or stable chlorine dioxide and water into the tank 1 to make them dissolved in the tank 1 thoroughly;
b. providing a tank 2, adding acidic substances, which can be dissolved in water and produce hydrogen ion in an aqueous solution, and water into the tank 2 to make

them dissolved in the tank 2 thoroughly;

c. providing a high pressure injection pump 3 which is provided with a water-feeding pipe 4 and a water-outgoing pipe 5; the said water-feeding water pipe 4 being directly connected with the tank 1, and connected with the tank 2 through a pressure pump 7 provided on the tank 2;

d. initiating the high pressure injection pump 3 and the pressure pump 7, making the solution in the tank 1 and the solution in the tank 2 entered into the high pressure injection pump 3 via the water-feeding pipe 4 and being pressured in the pump 3, then the mixed solution being entered into the oil (water) well 6 via the water-outgoing pipe 5 of high pressure injection pump 3, thereby the chlorine dioxide block-removing agent being synthesized in the well by the reaction between the chlorates and the acidic substances which can be dissolved in water and produce hydrogen ion in the aqueous solution.

According to the method of the present invention, wherein, the concentration of the aqueous solution of said chlorine dioxide block-removing agent synthesized in the well is controlled in the range of about 200mg/L to 5000mg/L.

According to the method of the present invention, wherein, the mix of the chlorate aqueous solution and acidic substances aqueous solution can be carried out at any position of the water-feeding pipe of the high pressure injection pump.

According to the method of the present invention, wherein, the said chlorate is selected from the group consisting of the chlorates of mono-valence and bi-valence metal cations and the chlorites of mono-valence and bi-valence metal cations, preferably sodium chlorate, potassium chlorate, sodium chlorite and potassium chlorite, and most preferably sodium chlorate and sodium chlorite.

In the method of the present invention, the hydrogen ion (H) in the solution is the necessary component for the formation of chlorine dioxide. According to the method

of the present invention, wherein, the said acidic substances are selected from the group consisting of the monoacids, biatomic acids and ternary acids which can be dissolved in water and can produce hydrogen ion, and the acid inorganic and organic salts which can be dissolved in water and can produce hydrogen ion.

According to the method of the present invention, wherein, the said monoacids include chloric acid, hydrofluoric acid, sulfamic acid, formic acid, lactic acid and acetic acid; the said biatomic acids include oxalic acid and tartaric acid; the said ternary acids include phosphoric acid and citric acid; the said acid salts include acid sulfate, acid phosphorate, acid carbonate and acid tartarate.

According to the method of the present invention, wherein, the acid is preferably phosphoric acid or acid salts of phosphorate, such as bi-sodium phosphorate, sodium phosphorate.

According to the method of the present invention, wherein, an expansion-preventing agent is further added into the solution of the acidic substances to prevent the expansion of clay, such as potassium chlorate or ammonia chlorate.

According to the method of the present invention, a corrosion inhibitor is further added into the solution of the acidic substances to prevent the corrosion of the pipes and the tanks, such as tri-sodium phosphate, sodium hydroxide or sodium tripolyphosphate.

According to the method of the present invention, a surfactant, preferably a non-ion surfactant, and sodium bicarbonate can be added.

According to the present invention, chlorate and acidic substances react each other in wells, then produce and release chlorine dioxide, so as to remove blocking. When sodium chloride is used as the chlorate and phosphoric acid or mono-sodium

phosphate is used as the acidic substance, the reaction equation is as follows correspondingly.

$$4H_3PO_4 + 5NaClO_2 = 4ClO_2 + 2H_2O + NaCl + 4NaH_2PO_4 \quad (1)$$

$$4NaH_2PO_4 + 5NaClO_2 = 4ClO_2 + 2H_2O + NaCl + 4Na_2HPO_4 \quad (2)$$

The equation of the formation of chlorine dioxide from the reaction of other chlorates or chlorites with other acidic substances is a common knowledge to the person skilled in the art, and it is not necessary to describe one by one.

According to the present invention, chlorate and acidic substances which can be dissolved in water and produce hydrogen ion in water react each other in wells, then produce chlorine dioxide step by step. Due to the strong oxidizing property of chlorine dioxide, it can to degrade various high molecular polymers, such as polyacrylamide, sesbania and guanidine etc., and to lower the viscosity thereof and to make them have good flowability. In the meantime, chlorine dioxide can quickly kill various microorganisms, such as sulfate-reduction bacteria, metatrophic bacteria and iron bacteria etc. Therefore, the objects of removing blocks in oil wells and water wells can be realized.

According to the method of the present invention, the quantity of chlorate can be calculated based on the quantity of chlorine dioxide needed in a well, and the above reaction equations (1) and (2).

The quantity of the acidic substances which can be dissolved in water and produce hydrogen ion can be calculated based on the quantity of sodium chlorite, and the above reaction equations (1) and (2).

The concentration of chlorine dioxide produced in a well is decided by the analysis of a working oil field based on the types of polymers and the degree of microorganism

blocks.

When operating an oil well, the total quantity of the block-removing agent (chlorine dioxide) to be injected can be calculated based on the following equation:

$$W_{\text{total quantity}} = \pi R^2 \cdot r \cdot H$$

Wherein,

W = the total quantity of the block-removing agent solution.

R = the radius of block-removing.

H = the thickness of the oil layer.

R = the porosity of the oil layer.

According to the method of the present invention, the concentration of chlorine dioxide formed in a well is controlled in the range of 200mg/L and 5000mg/L. The effect of block-removing would not be good if the concentration of chlorine dioxide is too lower, and the safety of working field could not be guaranteed if the concentration of chlorine dioxide is too high.

The present invention will be further described by the following example accompanying with the drawing.

According to the present invention, the procedures for the preparation of chlorine dioxide block-removing agent in an oil well and for the realization of block-removing comprise:

a. adding the main materials into the tank 1, and adding water into the tank 1 to make the main materials dissolved therein thoroughly;
b. adding the adjuvant materials (mainly the acidic substances which can be dissolved in water and produce hydrogen ion in an aqueous solution, and other

adjuvant materials, if necessary, such as expansion-preventing agent, such as potassium chloride or ammonium chloride; corrosion inhibitor, such as tri-sodium phosphate, sodium hydroxide or sodium tripolyphosphate; and surfactant and sodium bicarbonate etc.) and water into the tank 2 to make them dissolved in the tank 2 thoroughly;

c. connecting the tank 1 and the tank 2 with the water-feeding pipe 4 of the high pressure injection pump 3;
d. connecting the water-outgoing pipe 5 with the oil(water) well 6;
e. initiating the high pressure injection pump 3 and the pressure pump 7 at the same time, the solution of the tank 1 and the solution in the tank 2 whose quantity being controlled by the flow meter 8 being mixed and entered into the water-feeding pipe 4 of the high pressure injection pump 3, the mixture being pressured via the high pressure injection pump 3 and injected into the oil(water) well 6 via the water-outgoing pipe 5 of the high pressure injection pump 3;
f. a substitution solution being injected into the pipe in the well to expel the bock-removing agent solution therein into the oil layer after all the bock-removing agent solution having been injected into the pipe in the well, closing the well to make the bock-removing agent solution reaction in the well to realize the block-removing.

According to the present invention, the main materials mean chlorates, such as sodium chlorite.

For ordinary oil (water) wells, the period of closing is usually 24 hours. After that, the block-removing agent solution should be expelled out. After the expel of the block-removing agent solution, the well can start to work normally again.

According to the method of the present invention, the danger of explosion and the harm to human bodies due to the leak of chlorine dioxide can be avoided since the chlorine dioxide is prepared in the well. In the meantime, the corrosion of chlorine

dioxide to equipments and pipes is greatly decreased. The corrosion speed of chlorine dioxide to equipments and pipes is less than 15mg/m^2 • h.

EXAMPLE

The oil well No. F26-6 in Shengli Oil Field was an oil well with lower permeability. It was blocked. After blocked, the normal acidification block-removing method had been used to remove the blocking for several times. However, there were no any effects. Therefore, this well had been closed for one year and four months. Engineers in the working field think that, although there were some inorganic salts, the blocking mainly caused by the polyacrylamides and microorganisms accumulated at the area close to the bottom of the well. It was decided to remove the blockings by combining the normal acidification block-removing method with the method of the present invention. The inorganic salts blocking was removed by choric acid and hydrofluoric acid, and the polymer and microorganism blockings were removed by the method of the present invention. Based on the evaluation data made in a laboratory, it was considered that the concentration of chlorine dioxide block-removing agent in the well should be in the range of 1000mg/L-1200mg/L. According to the reaction equations (1) and (2), the quantity of sodium chlorite and the quantity of phosphoric acid were calculated out.

According to the thickness of the oil layer, the porosity and the radius of the block-removing, it had been calculated that, to remove the blockings of the oil well No. F26-6, 15m^3 aqueous solution of chloric acid and hydrofluoric acid was needed to remove the inorganic salts blocking. And 15m^3 of the block-removing agent aqueous solution of the present invention was needed to remove the polymer and microorganism blockings. For the preparation of the block-removing agent aqueous solution of the present invention, the solution of the main material (sodium chlorite) was made by dissolving 30 kg sodium chlorite in each of 1 m^3 water, and the amount of the adjuvant material (in view of phosphoric acid) was controlled by the flow meter

at a rate of 20 kg phosphoric acid per 1 m^3 of the solution of the main material. The main material and the adjuvant material were injected in the well continuously.

On July 10, 1999, the method of the present invention was carried out on the oil well No. F26-6 to realize the block-removing. After that, the oil output of the well F26-6 was increased from 0 to 405kg per day at the very beginning. The accumulated oil output was 1011 tons in one year. The effects of block-removing were shown in the following table.

Block-removing result of the oil well No. F26-6					
Year	Month	Moving Liquid Level	The output of oil (ton)	Water content	Remark
1998	2	2096	0.5	0.5	
	3	230 (static liquid level)		0.5	Occasional closed
	4				Occasional closed during April to June
	6	1870	4		Pump checking
					Closed during 98.7-99.6. The highest level of static liquid was 210 meters
1999	6				40m^3 sand was expelled, 3 broken oil pipes and 3356 scraped pipes were picked up using the block-removing agent in the present invention during the 7^{th}-10^{th}. Pump: 44/2099。
	7	2029	4.5	0.5	Pump: 44/2099
	8	1958	3.5	0.5	
	9	2010	3.1	0.5	
	10	372 (static liquid level)	2.4	0.5	The oil was flushed with 30m^3 water. One oil pipe was broken and was repaired. Pump: 44/2074
	11	1971	2.8	0.5	
	12	2028	2.1	0.5	
2000	1	2001	2.3	0.5	
	2	1768	2.6	0.5	
	3	1845	3.6	0.5	
	4	2033	3.5	0.5	During the 5^{th}-11^{th}, the pumps were checked and repaired.
	5	2068	3.3	0.5	

Remark: the above information is provided by shengli oil field.

According to the present invention, when the main reagent aqueous solution and the

adjuvant reagent aqueous solution are injected into a well, the enough concentration of the chlorine dioxide form based on the set up; without gas leaking, without explosion, without damage to people, simply application and safety. Because the quantity of produced chlorine dioxide can be controlled, and in a fixed time, the chlorine dioxide released continuously, therefore the ratio of removing blocks increases and the corrosion of chlorine dioxide to equipments and pipes decreases.